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RADIOCHEMICAL AND CHEMICAL CHARACTERIZATION OF SPENT MODERATOR RESIN FROM BRUCE NGS

REPORT NO. 91-27-K

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Water Research Unit
Process Chemistry Section
Chemical Research Department

ABSTRACT

Major chemical and radiochemical species found in a spent moderator ion exchange resin have been quantitatively identified. The normally expected corrosion products and deliberately added poison reagents have been found on the resin with cobalt-60 as the major contributor to the gamma field. Carbon-14 content was found to be comparable to those found previously for several similar resins. Presence of organically bound C-14 and H-3 has been inferred. Application of several new techniques has helped to increase the reliability and convenience of the resin characterization process. Several recommendations to improve the effectiveness of the programme are also suggested.

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31-102-462	837.812	March 15, 1991	91-27-K

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EXECUTIVE SUMMARY

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Spent ion exchange resins from the various purification circuits (PHT,Moderator, IFB, CAN-DECON) in Hydro's nuclear generating stations constitute a significant medium activity waste with a large disposal cost. A good knowledge of the chemical and radiochemical composition of the spent resins is an important prerequisite to effective planning of strategies on the handling, storage, disposal and long term stability of this voluminous solid waste.

As part of an on-going programme to address these needs, a spent moderator ion exchange resin from the Unit 4 of Bruce NGS has been analyzed. Cobalt-60, present at 2.7 μCi/mL, is the main long-lived contributor to the gamma field associated with the spent resin. Both cobalt and chromium have been found in particulate forms as well. Based on experimental determinations of C-14 and H-3 for individual components of the separated resin, values of 172 μCi /mL and 1.2 μCi/mL have been estimated for the C-14 and H-3 contents respectively of the mixed bed resin. There is some indication for the presence of organically bound tritium and C-14, and entrapped gaseous tritium.A new method based on inert sugar solutions has been successfully applied to separate the mixed bed resins into their components. Advantage has also been taken of resin combustion techniques to minimize the labour intensive analytical steps.

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RADIOCHEMICAL AND CHEMICAL CHARACTERIZATION OF SPENT MODERATOR RESIN FROM BRUCE NGS

S.A.Dias

1.0 BACKGROUND

Contaminated ion exchange resins constitute a significant medium activity waste generated during the operation of CANDU-PHW nuclear power stations. Yet, there are only limited data available on the chemical characteristics of waste ion-exchange resin materials. A comprehensive knowledge of their radiochemical and chemical composition is an essential pre-requisite for a sound programme of waste management dealing with the transportation /1/, storage, treatment and disposal /2/ of these resins. The growing importance of this type of information was recently highlighted by several incidents /3/ of exothermic reactions involving dewatered ion-exchange resins, that occurred both during the dewatering process and during transport to the disposal site in the U.S.A. An on-going programme /4/ at the Research Division aims to generate this information through a systematic sampling and characterization scheme.

The purpose of this study was to extend the data base on chemical and radiochemical characteristics of Hydro's spent ion-exchange resins. Presented in this report are the results of laboratory experiments to characterize a representative sample of a spent moderator ion exchange resin from Bruce NGS.

2.0 SAMPLE DESCRIPTION

A sample of about 80 mL from Bruce NGS Unit 4 (IX3) moderator system collected on September 26, 1989, using the Research Division resin slurry sampler, was received at the RML with a contact field of about 300 mR/h at the middle of the lucite sampler. The highest contact radiation field on the enveloping "lead castle" was about 30 mR/h, near the bottom. The corresponding field on the outside of the metal drum enclosing the "castle" was 3 mR/h, near the middle. The point of sampling was in the slurry line carrying the spent resin from the chariot vessel to the dedeuteration tank. Heavy water had been used throughout all the slurry operations. The sample of resin thus collected was dedeuterated at the station with about 10BV of regular DI water.

The resin originated from the IX 3 column and no information is available on its service history. The resin had been slurried to the chariot vessel one day before the sample collection date.

3.0 PRELIMINARY EXAMINATIONS

In an attempt to remove any residual tritium(H-3), the entire sample was dedeuterated with 1142 mL (14.3BV) of DI water which released a total of 546 mCi of H-3. A further dedeuteration with methanol in a Soxhlet apparatus resulted in the release of another 159 μCi of H-3 and the off-gases not condensed by the water condenser had an activity of 297.5 nCi of H-3.

4.0 ANALYSIS AND OBSERVATIONS

The analytical protocol used is given in Appendix 1. After dedeuteration of the sample again, at the OHRD laboratories to almost constant tritium activity, two sub-samples of 5mL and 10mL were removed for detailed chemical analysis. As a result of the agitation and the dedeuteration operation at the station, there was no visible non-resin particulate matter in the original slurry water. In an attempt to get more information on the speciation of contaminants on the resin, parallel analysis was performed on separated anion and cation components of the original mixed bed resin. Manual separation of the mixed bed resin following selective colouration with a chemical dye was found to be too tedious to obtain large enough samples. Hence, a new method using aqueous sugar solutions was developed and successfully used in this work. This method was found to be faster and afforded a much cleaner separation. It is planned to describe the details of this method in a separate report.

Resin destruction to determine the organically bound C-14 was achieved by combustion in an oxygen bomb containing a little DI water at the bottom. This method,additionally,has the potential of revealing the composition of the original resin, other than carbon, hydrogen,and oxygen,through ion-chromatography (inorganic anion peaks) of the water solution remaining in the bomb. Thus, by determining the amount of sulphate and nitrate, which are derived from the functional groups of the resin, a quantitative estimate of resin degradation due to radiation and thermal effects may be ascertained. Addition of an oxidizing agent to the original water might increase the recoveries of the combustion products of active sites in the resin.

5.0 RESULTS AND DISCUSSION

Gamma activities were decay-corrected to September 26, 1989 and are only reported for determinations with less than 40% uncertainty (2 sigma values) in counting. The concentrations of analytes reported on a volume basis (mL) are for completely water swollen wet resin (gravity settled beads), and those reported on a weight basis are for air-dried resin beads.

5.1 Residual Tritium

In spite of an initial dedeuteration with 10BV of light water at the station, a total of 6.8 mCi of tritiated water was immobilized on the resin. This water seems to be very tenaciously held within the beads and part of this water is released only under extreme conditions such as with the azeotropic solvents used in this work. The non-condensable tritium activity (3.7nCi/mL) released during azeotropic dehydration is likely to be tritiated gases, possibly trapped within the beads. Thus, it appears that the dedeuteration performed under field conditions may not be complete.

5.2 Original Slurry Water

The water (93mL),in which the resin was transported to the Radioactive Materials Laboratory (OHRD), was found to contain 8mCi/mL of H-3 that had diffused out after the initial dedeuteration The gamma activity in this water (Table 1) was low with the largest contribution from Co-60 followed by Cr-51.

Table 1
Gamma Activity in Slurry Water

RADIONUCLIDE	ACTIVITY (nCi/mL)
Co-60	57
Cr-51	30
Nb-95	5.3
Tb-160	2.4
Gd-153	2.1
Fe-59	1.8
Mn-54	1.0
Co-58	0.7

Almost all of this activity was retained on a 0.2μm filter , thus indicating that these corrosion products are present in particulate forms or adsorbed on particulates in the water.

5.3 Ultrasonic Treatment

The entire resin sample was subjected to an ultrasonic treatment in a column containing 130 mL of DI water. The slurry water after filtration through 0.2μm filters produced little or no gamma emitting nuclides but possessed a tritium activity of 20 nCi/mL corresponding to a total of 2.6μCi. The filterable residue had Cr-51 and Co-60 as the principal gamma emitters (Table 2).

Table 2

Gamma Emitting Nuclides on Solid Residue Dislodged by Ultrasonic Treatment

RADIONUCLIDE	ACTIVITY (μCi)
Co-60	73
Cr-51	92
Nb-95	29
Tb-160	32
Sb-125	1.9
Fe-59	7.5
Mn-54	4.5
Sc-46	9
Co-58	1.2

Thus, it appears that a certain amount of activated corrosion products associated with the ion exchange resin are not found in an ionic form but loosely embedded in the bead surface.

5.4 Solid State Gamma Analysis

After removal of exchangeable water and the ultrasonic treatment, the resin sample was subjected to detailed gamma analysis. The results are given in Table 3 and they probably represent the total immobilized activity on the resin.

Table 3

Gamma Emitting Nuclides on the Resin

RADIONUCLIDE	HALF-LIFE	RELATIVE CONTRIBUTION TO GAMMA FIELD (%)	ACTIVITY (μCi/mL)
Co-60	5.3 y	42	2.7
Cr-51	28 d	0.70	0.35
Nb-95	35 d	0.48	0.1
Tb-160	73 d	37	2.7
Zn-65	244 d	0.70	0.1
Fe-59	45 d	-	BD
Mn-54	312 d	3.6	0.7
Sc-46	84 d	0.37	0.03
Gd-153	242 d	15	11.7
Co-58	71 d	0.10	0.02

As can be seen, gadolinium is the chief contributor to the activity while cobalt, with its high gamma energy, is the single most important long-lived contributor to the gamma field. Traces were also found of most of the usual activated corrosion products of Bruce NGS moderator system materials. Interestingly, the amount of corrosion products on this resin seems to be significantly lower than those found /5/ on a similar spent resin from Unit 2 moderator system of the same station.

5.5 Removal of Bead Water

Attempts were made to completely dewater the resin beads to determine the last trace of chemically unbound tritium. Firstly, the entire 5 mL of the dedeuterated resin was extracted with methanol. This treatment released a total of 10 nCi of tritium and 0.02 μCi of C-14. The minute amount of C-14 released must be due to thermal stripping by boiling methanol (b.p. 64.5°C). In another attempt, a separate sample of the dedeuterated resin (5mL) was refluxed with dry toluene using a Deen's trap to azeotrope the residual water. The amount of water recovered and its tritium content are 3.5 mL and 29 μCi respectively. Thermal desorption by boiling toluene (b.p. 111°C) resulted in the evolution of carbon dioxide containing 175 nCi of C-14.

5.6 Resin Combustion / C-14 Determination

A batch of the original resin was separated into its constituent anion and cation resins and a sample of each was combusted in a tube furnace to determine the total C-14 content. The ash produced from each sample was gamma analyzed and the results are given in Table 4.

Table 4

Gamma Emitting Nuclides on Ash Residue from Combustion

RADIONUCLIDE	ASH FROM ANION RESIN nCi/g, resin	ASH FROM CATION RESIN nCi/g, resin
Co-60	55.5	10900
Cr-51	462	138
Nb-95	6.28	664
Gd-153	80.5	128000
Mn-54	15.3	6060
Tb-160	26.9	30100
Sb-125	27.4	BD
Sc-46	9.05	105
Co-58	BD	121
Ce-141	0.39	144
Eu-154	BD	6970
Zn-65	BD	1040

These results show the different distribution of various metal ions on the cation and anion resins - particularly noteworthy is the distribution of cobalt and gadolinium. Cobalt seems to be associated with both anion and cation resins in an approximate ratio of 1:200 whereas gadolinium is largely on the cation resin. Antimony, as seen before , is found exclusively on the anion resin.

This combustion produced a total of 727 μCi/g of C-14 and 4.4 μCi/g of tritium from the anion resin. The corresponding numbers for the cation resin are 1.3 μCi/g and 1.0 μCi/g respectively. While C-14 appears to be associated largely on the anion resin, the small amount found on the cation resin could, perhaps, include both organically bound species as well as those, such as carbon monoxide and carbonates that are directly complexed with the metal ions. In a separate series of determinations, using hydrochloric acid stripping /6/, values for C-14 ranging from 41 to 66.6μCi/mL and 1μCi/mL of H-3 have been found for the mixed bed resin. On a weight basis, the combustion techniques produced values of 36.0μCi/g for C-14 and 1.4 μCi/g for H-3 when a sample of the original mixed bed resin was used. These values do not approximate to the corresponding values on a volume basis and thus indicate the non-representative nature of the sub-samples. For these reasons, perhaps, a more realistic value may be obtained by extrapolating the values for the separated anion and cation components to an isoequivalent mixture. Using the experimentally determined conversion factors of 1g (dry)≡2.66mL (wet) for the cation , and 1g ≡ 2.63mL for the anion resin, the estimated C-14 and H-3 contents of the mixed bed resin would be 172 μCi/mL (wet) and 1.2 μCi/mL (wet) respectively. This C-14 value is comparable with those reported /7,8/ for several other moderator resin samples from Bruce NGS.

In a separate experiment, the cation resin was combusted in a muffle furnace using a platinum crucible, followed by lithium tetraborate fusion and dissolution in hydrochloric and nitric acids to prepare a solution of the metal loading. The resultant solution was then analyzed by atomic absorption spectroscopy and the results are given in Table 5.

Table 5

AA Analysis of Cation Resin

Species	Concentration (μg/g resin)
Co	less than 20
Cr	less than 51
Mn	less than 10
Fe	184
Ni	20

Thus, it can be seen that the amount of inactive transition metal species found on the cation resin is relatively very large compared to their active counter parts, with iron species being the most predominant. These are all obviously corrosion products from materials of construction.

5.7 Anion Analysis

The anions on the anion resin were eluted in a column using the special reagent Tiron ® (*4,5 - dihydroxy- 1,3 - benzenedisulphonic acid disodium* salt) and the collected effluent was analyzed by ion chromatography. The results from this analysis are summarized in Table 6.

Table 6

Anions by Ion Chromatography

Analyte	Concentration on resin (ppm, wet)
F^-	less than 72
Cl^-	102
NO_3^-	338
PO_4^{3-}	less than 0.3
SO_4^{2-}	78

The chloride found on the resin could be the residual chloride from the chloromethylation reaction used for functionalizing the anion resin during resin manufacture. The nitrate is ,of course, largely from the gadolinium nitrate poison and, as would be expected, is the major anionic species. At least in principle, the nitrate could arise from several other sources as well. It could arise from nitric acid used for slight acidification of the moderator water prior to a guaranteed shut-down. Another likely source is the radiolytic production from ingressed air (air in-leakages) into the moderator system cover gas. And thirdly, derivation of nitrate from radiolytic decomposition of the anion resin is also a possibility. The relatively low level of gadolinium on the resin suggests that this resin

probably was not used for pulling gadolinium after reactor shut-down and as such, nitric acid addition as a source may be ruled out. The origin of sulphate is likely to be from resin disintegration involving cation resin. The radiolytic and oxidizing environment within the resin bed ,from buildup of radioactive materials there, is conducive to resin degradation. Radiolysis of ion exchange resins used in the purification systems of Savannah River reactors became apparent when S-35 ($t_{1/2}$ = 87.2 d) and P-32 ($t_{1/2}$ = 14.3 d) ,and sulphate ion were found in the D_2O coolant-moderator system. The S-35 and P-32 were attributed /9,10/ to neutron activation of natural sulphur released from the cation resin that was used to supplement the mixed beds in the purification of the moderator water.

The boron content of the resin was determined in a separate analysis (ICP) to be 2.0 mg of B (or 10.8 mg as BO^{3-}_3) per mL of air - dried resin and as would be expected,it was found exclusively on the anion resin.

5.8 Neutron Activation Analysis

Several samples generated during the course of the resin separation and analysis were subjected to neutron activation analysis and the results are given in Table 7.

Table 7

Neutron Activation Analysis Data
Results expressed in μg/g air-dried resin

Sample	Na	Sc	Sb	Cr	Co
Anion resin	110	<0.02	0.07	<10	<5
Cation resin	<50	<0.03	<0.08	<10	<10
Anion resin after Tiron®	20800	<0.03	<0.08	6	Not Detected
Cation after HCl stripping	520	0.001	0.02	2	0.2
Anion after HCl stripping	30	0.001	0.02	12	1.0

The high values of sodium in the anion resin and in the acid stripped cation resin are, probably, due to contamination as suggested by coexistence of bromide in the samples- presumably from masking tape used during sample preparation. The exceedingly high sodium value in the Tiron® stripped-resin is almost certainly due to the residual sodium from the stripping reagent. It can also be seen that the powerful anionic reagent, Tiron®, leaves only half the amount of chromium left behind by hydrochloric acid used for stripping the anion resin. This would be expected if the chromium is present on the anion resin as either bivalent chromate or dichromate ion, for both of which the resin has a high affinity. The Incoloy-800 heat exchanger tube materials in the Bruce NGS moderator system nominally contain 21% chromium and with a large surface area would be a major source of chromium. Chromium could easily be oxidized to chromate and dichromate ions by species such as peroxides likely to be found in the aqueous medium. No nickel or iron was discerned in this analysis in spite of their contribution of about 38 and 33% respectively to the hardware composition, thus suggesting differential attacks by moderator water.

6.0 SUMMARY AND CONCLUSIONS

A detailed characterization of a spent moderator resin has been carried out.

The normal procedure used for dedeuteration of the contaminated resin leaves a small amount of tritium behind on the resin. There is some indication for the presence of organically bound tritium and C-14, and entrapped gaseous tritium.

A new method based on sugar solutions has been successfully applied to separate the mixed bed resins into their components. This method does not seem to produce unwanted elutions of contaminants from the resin and therefore should be used in future resin analyses.

The resin combustion technique affords a convenient and rapid method for sample preparation for chemical analysis and should be explored for elemental analysis of the resin matrix

Cobalt-60, present at 2.7μCi/mL, is the main long-lived contributor to the gamma field associated with the spent resin. Both cobalt and chromium have been found in particulate forms as well. The speciation of several corrosion products may be inferred from resin separation studies. Relatively large amounts of inactive cationic and anionic species associated with the resin have also been found.

Based on experimental determinations of C-14 and H-3 for individual components of the separated resin, values of 172 μCi /mL and 1.2 μCi/mL have been estimated for the C-14 and H-3 contents respectively of the mixed bed resin.

7.0 RECOMMENDATIONS

1. It is recommended that the present programme be continued to permit characterizations of more resin samples to expand the existing data bank to make it more reliable.

2. It is recommended that stations which have undertaken resin sampling should incorporate a standard procedure into their work plans.

3. Resin sampling should be done as soon as possible after the ion exchange columns have been valved out of service, in order to ensure detection of short-lived isotopes.

4. To obtain better evaluation of the performance of resins in station purification systems, and also to warrant more detailed characterization of the resin, the following are recommended:

   (a) A small sample (1L) of unused resin should be collected and retained from the same lot as used in service columns.

   (b) The full service period of all resin columns together with the information from the suppliers should be recorded.

8.0 ACKNOWLEDGEMENTS

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REFERENCES

1. "Radionuclide Characterization For RFTP Shipments", Sullivan, G.J., Memorandum to Mr. J. Harjula (NED),CPS-00531.1-02 (T10), November 6, 1989.

2. "The Low Level Radioactive Waste Disposal Development Program 1987-1992", Dalziel,B.P.,Ontario Hydro Nuclear Materials Management Department Report No. 88249, March 1988.

3. "Technical Consideration Affecting Preparation of Ion-Exchange Resins for Disposal", Bowerman, B.S., and Piciulo, P.L., 1986, NUREG/CR-4601.

4. "Analysis of Spent Ion Exchange Resins from Pickering GS", Dias,S.A.,Ontario Hydro Research Report No. C88-79-K.

5. "Radiochemical Analysis of Spent Moderator Resin from Bruce NGS", Dias,S.A.,Ontario Hydro Research Report No. C87-53-K.

6. "C-14 Removal from Spent IX Resins - Phase III : Operation of a Pilot Scale Reactor",Chang,F.H., Ontario Hydro Research Division Report No. 91-19-H.

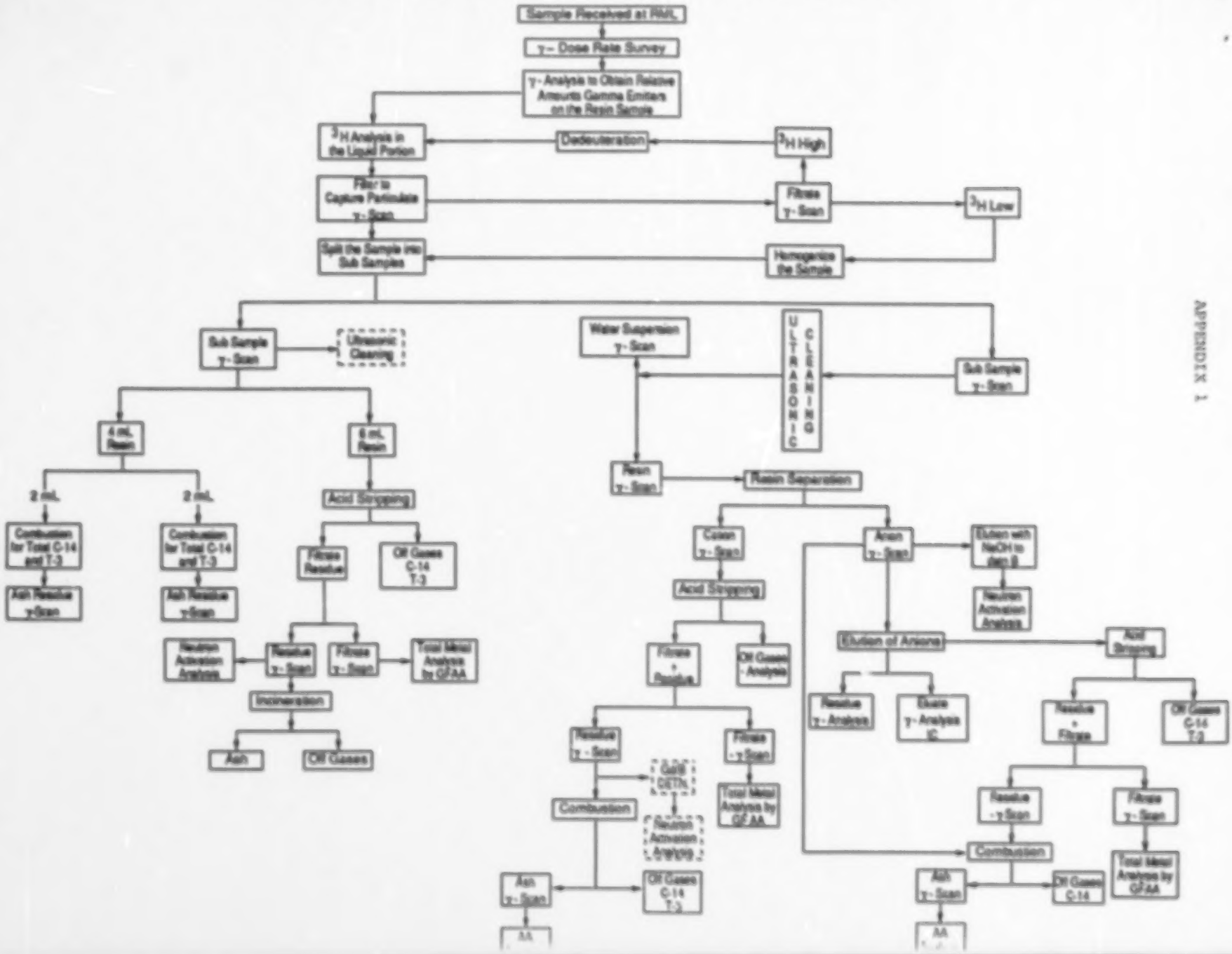
7. "Decontamination of Spent Moderator Resin from Pickering NGS 'A' ", Nott, B.R., Ontario Hydro Research Division Report No. 80-30-K.

8. "Characterization and Regeneration of PNGS 'A' Moderator Anion Resin", Nott, B.R., Ontario Hydro Research Division Report No. 80-448-K.

9. "Radiolysis of Ion Exchange Resins Used in the Purification Systems of Savannah River Reactors", Baumann, E.W., E.I. Du Pont De Nemours & Company Report No DP-977, July 1965,{ Contract AT (07-2)-1 with the United States Atomic Energy Commission }.

10. "Effects of Oxidation on Ion Exchangers",Wirth, L.F., Feldt, C.A., and Odland, K., Industrial Engineering and Chemistry,53, 638-41, (1961).

ANALYTICAL PROTOCOL FOR SPENT MODERATOR IX RESINS



APPENDIX I